

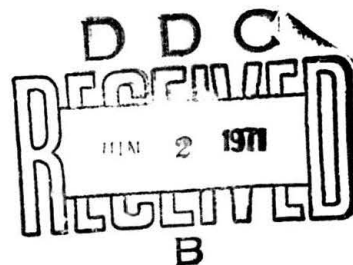
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RAMAN BANDSHAPES AND ROTATIONAL DIFFUSION OF MOLECULES

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RAMAN BANDSHAPES AND ROTATIONAL DIFFUSION OF MOLECULES*

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Summary

It has been shown that the shapes of vibrational Raman bands, measured with both parallel and crossed nicols, may serve as a tool for the study of the reorientation of rigid molecules (or molecular fragments) even if other line-broadening mechanisms are not negligible. The theory, developed for the case of isotropic media (including dense gases, liquids, and some molecular solids), holds independently of the shape of the molecules; the only requirement is that the studied band must be related to a vibration which is sufficiently localized to the individual molecule (molecular fragment).

Any vibrational Raman band provides, in principle, enough information for a complete characterization [by means of a correlation function $\chi(\underline{\alpha}^{rs}; \tau)$] of the reorientation of the corresponding transition polarizability tensor $\underline{\alpha}^{rs}$. An exhaustive characterization of the reorientation properties of all second-rank molecular quantities is shown to be probably out of the reach of Raman spectroscopy except when the molecule (molecular fragment) has a high symmetry and/or a specific model of the reorientation process is accepted.

The shapes of vibrational Raman bands contain a considerable amount of information about the rotational diffusion and other random processes, the knowledge of which is badly needed as a starting point for the construction of an acceptable model of the structure of liquids and dense gases. This fact is widely known and some effort to exploit the Raman band-shapes has already been expended.

The theory of Raman effect, including the rotational structure of a vibrational Raman band in the case of a free molecule, has been well established¹ since 1932. For a long time, however, there had not been any real need for a good theory of the lineshapes because of the poor quality of the Raman spectra. Recently this situation changed drastically as a consequence of the introduction of laser sources of excitation radiation.

The problem of the shapes of Raman lines has been treated by Gordon²⁻⁴. Unfortunately, Gordon's results hold only for the perpendicular bands of highly symmetrical molecules under the independent condition that rotational diffusion is the dominant broadening mechanism.

In a certain sense, this paper is an extension of the Gordon's approach to the case of a general-shape molecule participating in several qualitatively different relaxation mechanisms.

Although this paper is of a theoretical character, the experimental limitations have been taken into account throughout its development. The possibilities discussed from the theoretical point of view are all experimentally feasible (at least in principle); the technical requirements connected with them can be met assuming that adequate care is being paid to the geometry of the measuring apparatus.

I. Basic Theory

The intensity of a vibrational Raman band is due to the oscillating component \underline{D}^{rs} of the induced dipole moment, the form of which is

$$\underline{D}_{\alpha}^{rs} = E \underline{A}_{\alpha\beta}^{rs} \underline{\epsilon}_{\beta} \cos[2\pi(\nu_e - \nu_{rs})t - \underline{k} \cdot \underline{R}_{\alpha}] \quad , \quad (1)$$

where \underline{A}^{rs} is the transition polarizability tensor⁵ of the molecule, \underline{R} is the position vector of its center of mass, ν_{rs} is the energy difference between the vibrational levels r and s expressed in frequency units, and E , \underline{k} , $\underline{\epsilon}$, and ν_e are the amplitude, wave vector, polarization, and frequency, respectively, of the excitation light wave.

The flux of the radiation energy emitted by \underline{D}^{rs} in the direction $\underline{\tau}$ with the polarization $\underline{\chi}$ is then given as⁶

$$I^{rs} = c_r (\nu_{rs}^0)^4 \underline{A}_{\gamma\mu}^{rs} \underline{A}_{\delta\varphi}^{sr} \frac{\delta\alpha\gamma}{\delta\beta\delta} \underline{\tau}_{\alpha} \underline{\tau}_{\beta} \underline{\chi}_{\gamma} \underline{\chi}_{\delta} \underline{\epsilon}_{\mu} \underline{\epsilon}_{\varphi} \quad , \quad (2)$$

where

$$c_r = 2N_r (\pi/c)^3 E^2 \quad \text{and} \quad \nu_{rs}^0 = \nu_e - \nu_{rs} \quad ,$$

N_r being the number of molecules which are in the vibrational state r .

Eq. (2) holds only for an isolated, space-fixed molecule. In order to generalize it, let us first notice that Eq. (1) may be rewritten in such a way that the molecular parameters \underline{A}^{rs} and \underline{R} appear in a single term denoted as $\underline{Q}^{rs} = \underline{A}^{rs} \exp(2\pi i \underline{k} \cdot \underline{R}_{\alpha})$. In any realistic case, \underline{Q}^{rs} is a time-dependent quantity, the three major sources of this time-dependence being: molecular rotation (both overall and internal), molecular translation, and any kind of vibrational energy transfer which terminates the existence of the molecule in any one of the vibrational states r and s .⁷ In all physically feasible cases the time dependence is of a stationary random type and may be characterized by suitable correlation functions. The secondary emission due to \underline{D}^{rs} then gives rise to a continuous band of frequencies centered around the frequency ν_{rs}^0 . The intensity profile of the band may be obtained straightforwardly either as a

Fourier transform of the radiation emitted by \underline{D}^{rs} (classical approach), or directly from first principles using any of the general techniques of quantum mechanics. The resulting formula reads

$$I^{rs}(\nu) = c_r(\nu_{rs}^0 - \nu)^4 \frac{\delta_{\beta\delta}^{\alpha\gamma}}{\tau_\alpha \tau_\beta \tau_\gamma \tau_\delta} \epsilon_\mu \epsilon_\nu \int_{-\infty}^{+\infty} \exp(-2\pi i \nu \tau) \underline{G}_{\gamma\mu, \delta\varphi}^{rs}(\tau) d\tau \quad (3)$$

The explicit form of the correlation tensor $\underline{G}^{rs}(\tau)$ is

$$\underline{G}_{\gamma\mu, \delta\varphi}^{rs}(\tau) = \mathcal{A} \{ \underline{A}_{\gamma\mu}^{rs}(t) \underline{A}_{\delta\varphi}^{sr}(t+\tau) \exp[2\pi i k_\alpha [R_\alpha(t) - R_\alpha(t+\tau)]] \} \quad (4)$$

The ensemble averaging \mathcal{A} involves the evaluation of a weighted trace of the quantity $[\underline{Q}^{rs}(t) \underline{Q}^{sr}(t+\tau)]$ over the configuration space of all degrees of freedom except the vibrational ones⁸. The weight factor is given by an effective Boltzmann operator⁹. Once this factor is introduced, the Hermitian character of the traced operator is lost and $\underline{G}^{rs}(\tau)$ becomes complex.

Equation (3) is valid only under the assumption that the vibrational degrees of freedom are not coupled to the remaining ones. This is obviously not always true since at least the vibration-rotation interactions are often strong enough to be observed. However, the interactions of this kind influence mainly the asymmetry of the band while the symmetrical part (defined as $I_{\text{sym}}^{rs}(\nu) = \frac{1}{2}[I^{rs}(\nu) + I^{rs}(-\nu)]$) is almost insensitive to them. The error caused by neglecting such perturbations is thus expected to be concentrated in the complex part of \underline{G}^{rs} while the real part remains much more reliable. Fortunately, the real part is strongly dominant in all practical cases.

II. Experimental Determination of the Correlation Tensor

An a priori calculation of $\underline{G}^{rs}(\tau)$ is undoubtedly far beyond the reach of today's theoretical methods. However, the use of lasers led to such an improvement in the quality of Raman spectra that the measurement of natural lineshapes became quite feasible. Let us therefore see how much information about the tensor $\underline{G}^{rs}(\tau)$ may be obtained experimentally by assuming that the natural shapes of vibrational bands can be measured exactly.

Although $\underline{G}^{rs}(\tau)$ is a fourth-rank tensor, its 81 components are to a large extent interconnected by various symmetry requirements. First of all, \underline{A}^{rs} is a symmetrical tensor so that, by (4),

$$\underline{G}_{\alpha\beta,\gamma\delta}^{rs}(\tau) = \underline{G}_{\beta\alpha,\gamma\delta}^{rs}(\tau) = \underline{G}_{\alpha\beta,\delta\gamma}^{rs}(\tau) = \underline{G}_{\beta\alpha,\delta\gamma}^{rs}(\tau) \quad (5)$$

for all α, β, γ , and δ . Further, $I^{rs}(\nu)$ must be real which implies

$$\underline{G}_{\alpha\beta,\gamma\delta}^{rs}(\tau) = \underline{G}_{\alpha\beta,\gamma\delta}^{rs*}(-\tau) \quad (6)$$

Combined with (4), this gives

$$\underline{G}_{\alpha\beta,\gamma\delta}^{rs}(\tau) = \underline{G}_{\gamma\delta,\alpha\beta}^{rs}(\tau) \quad (7)$$

Even in the most general case, Equations (5) and (7) allow for only 21 independent components. A further simplification results when one considers a macroscopically isotropic sample for any quantity obtained through the ensemble averaging \mathcal{A} must respect the macroscopical symmetry of the sample independently of the symmetry of the constituent molecules. The components $\underline{G}_{\alpha\beta,\gamma\delta}^{rs}(\tau)$ must then be invariant with respect to any permutation of the coordinate axes. This condition reduces the number of independent components to the following six:

$$\underline{G}_{XX,XX}^{rs} ; \quad \underline{G}_{XY,XY}^{rs} ; \quad \underline{G}_{XX,YY}^{rs} ; \quad \underline{G}_{XX,XY}^{rs} ; \quad \underline{G}_{XX,YZ}^{rs} ; \quad \underline{G}_{XY,XZ}^{rs} .$$

Since the properties of an isotropic sample are invariant with respect to any mirror reflection, the last three of these coefficients must be identically zero.

Let the Z-axis of the laboratory system of coordinates be oriented along $\underline{\tau}$, i.e., in the direction of the scattered radiation which is observed. For any directions of the vectors $\underline{\varepsilon}$ and $\underline{\mathcal{K}}$ ($\underline{\mathcal{K}} \perp \underline{\tau}$) there exists a realizable experimental arrangement characterized by a scattering angle and by the orientations of the nicols defining the polarizations of the incident and scattered light-waves. From the shape of the band, $I^{rs}(\underline{\varepsilon}, \underline{\mathcal{K}}; \nu)$, measured at this arrangement, the function

$$G^{rs}(\underline{\varepsilon}, \underline{\mathcal{K}}; \tau) = \underline{G}_{\alpha\beta, \gamma\delta}^{rs}(\tau) \varepsilon_{\alpha} \varepsilon_{\beta} \mathcal{K}_{\gamma} \mathcal{K}_{\delta} \quad (8)$$

can be easily obtained by means of an appropriate Fourier transform of Equation (3). The two simplest arrangements lead to the correlation functions

$$G_1^{rs}(\tau) = G^{rs}(1, 0, 0; 1, 0, 0; \tau) = \underline{G}_{XX, XX}^{rs}(\tau) \quad (9a)$$

and

$$G_2^{rs}(\tau) = G^{rs}(1, 0, 0; 0, 1, 0; \tau) = \underline{G}_{XY, XY}^{rs}(\tau) \quad (9b)$$

The experimental results must remain unchanged if the laboratory system of coordinates is rotated around the Z-axis. Applied to Eq. (9a), this principle gives

$$G^{rs}(2^{-\frac{1}{2}}, 2^{-\frac{1}{2}}, 0; 2^{-\frac{1}{2}}, 2^{-\frac{1}{2}}, 0; \tau) = \frac{1}{2}(\underline{G}_{XX, XX}^{rs} + \underline{G}_{XX, YY}^{rs}) + \underline{G}_{XY, XY}^{rs} = \underline{G}_{XX, XX}^{rs}.$$

In consequence,

$$\underline{G}_{XX, YY}^{rs}(\tau) = \underline{G}_{XX, XX}^{rs}(\tau) - 2\underline{G}_{XY, XY}^{rs}(\tau).$$

The two experimentally accessible correlation functions G_1^{rs} and G_2^{rs} thus completely determine the whole correlation tensor \underline{G}^{rs} provided that the sample is isotropic.

III. Decomposition of the Correlation Tensor

It is reasonable to assume that the cross-correlation between various qualitatively different random processes is practically negligible. This assumption enables one to write (4) in the form

$$\begin{aligned}\underline{g}^{rs}(\tau) &= c_{rs}(\tau) \underline{c}^{rs}(\tau), \\ c_{rs}(\tau) &= \bar{c}^d(\tau) \bar{c}_r^v(\tau) \bar{c}_s^v(\tau),\end{aligned}\quad (10)$$

where $\underline{c}^{rs}(\tau)$ includes the processes which influence either the shape or the orientation of the polarizability ellipsoid, and $\bar{c}(\tau)$ are the reduced correlation functions describing the remaining random processes which will now be discussed in more detail.

III.1. Translational diffusion (d).

The translational diffusion affects the Raman band shapes through the exponential term in (4). The corresponding reduced correlation function has the form

$$\bar{c}^d(\tau) = \mathcal{A}_{tr} \{ \exp(2\pi i k_{\alpha} [R_{\alpha}(t) - R_{\alpha}(t+\tau)]) \} . \quad (11)$$

Because of its dependence on the wavelength of the incident light, the translational diffusion can always be distinguished experimentally. If the shape of a band has been measured at several wavelengths, the corresponding correlation functions can be extrapolated to $\lambda = \infty$; this is equivalent to putting $\bar{c}^d(\tau) = 1$. For a given λ , $\bar{c}_{\lambda}^d(\tau)$ is then equal to the ratio of the actual correlation function to the extrapolated one.

In low-density gases, where the free path of the molecules exceeds substantially the wavelength of the excitation light, $\bar{c}^d(\tau)$ can be easily calculated. The result is of course equivalent to any other

description of Doppler broadening. In the region where Doppler broadening is a dominant feature, the width of the lines are typically of the order of 0.01 cm^{-1} . At higher densities the free path of the molecules becomes comparable to or smaller than the wavelength of the excitation light and the theory of Brownian motion must be applied in order to calculate the values of $\bar{C}^d(\tau)$.

In the dense gases and liquids to which Raman spectroscopy may easily be applied, the collisions between molecules are so frequent that the Doppler-broadening contribution is almost 'quenched' and negligible with respect to the other broadening mechanisms.

III.2. Vibrational energy transfer (v)

The correlation function $\bar{C}_r^V(\tau)$ includes all types of the vibrational energy transfer and may be approximated as

$$\bar{C}_r^V(\tau) = \exp(-\tau/\tau_r^V) \quad , \quad (12)$$

where τ_r^V is the mean lifetime of the vibrational state r . With respect to what has been said about translational diffusion, the factors $\bar{C}_r^V(\tau)$ and $\bar{C}_s^V(\tau)$ determine the time dependence of $C_{rs}(\tau)$ in practically all real cases.

If r denotes the ground state and s an excited vibrational state, then, because of the thermal distribution requirements, $\tau_s^V < \tau_r^V$. This means that if the vibrational frequency ν_{rs} is large enough to satisfy the condition $\exp(-\nu_{rs}/kT) \ll 1$, the time-dependence of $C_{rs}(\tau)$ is almost completely dominated by $\bar{C}_s^V(\tau)$.

The importance of the vibrational energy transfer as a broadening mechanism increases very quickly with the size of the molecule because of the increasing density of its vibrational states. On the other hand, the effectiveness of the rotational diffusion decreases with increasing

size of the molecule. One must therefore expect that rotational diffusion, which has been shown² to be the dominant broadening mechanism for several small molecules, might be only a secondary effect for anything larger than the molecule of methane.

III.3. Variations of the polarizability tensor due to intermolecular interactions

The tensor $\underline{c}^{rs}(\tau)$, mathematically defined as

$$\underline{c}_{\alpha\beta, \gamma\delta}^{rs}(\tau) = \mathcal{A} [\underline{a}_{\alpha\beta}^{rs}(\tau) \underline{a}_{\gamma\delta}^{sr}(t+\tau)] , \quad (13)$$

may be decomposed into two terms, one of which regards only the pure rotational diffusion of the average-shape polarizability ellipsoid, while the other, supposedly small in comparison with the first, includes also the random variations of molecular polarizability arising from intermolecular interactions.

Let \underline{a}^{rs} be the average polarizability tensor of a molecule in the sample. The actual polarizability tensor of such a molecule differs from \underline{a}^{rs} by a value $\underline{b}^{rs}(t)$. Both of these quantities are then subject to the overall rotations of the molecule. This decomposition transforms Eq. (13) into

$$\underline{c}^{rs}(\tau) = \underline{s}^{rs}(\tau) + \underline{w}^{rs}(\tau) ,$$

where

$$\underline{s}_{\alpha\beta, \gamma\delta}^{rs}(\tau) = \mathcal{A}_{\text{rot}} [\underline{a}_{\alpha\beta}^{rs}(t) \underline{a}_{\gamma\delta}^{sr}(t+\tau)] ,$$

and

$$\underline{w}_{\alpha\beta, \gamma\delta}^{rs}(\tau) = \mathcal{A} [\underline{b}_{\alpha\beta}^{rs}(t) \underline{b}_{\gamma\delta}^{sr}(t+\tau)] . \quad (14)$$

Unfortunately, no theory exists which would permit one to calculate the tensor $\underline{w}^{rs}(\tau)$. An estimate can be made taking into account only the electrostatic interactions between molecules. Then the variations of the molecular polarizability may be considered as due to the fluctuating

electric field $\underline{e}(t)$ caused by the presence and motion of other molecules. The first-order Taylor expansion of the dependence of \underline{A}^{rs} on the applied electric field is

$$\underline{A}_{\alpha\beta}^{rs} = \underline{a}_{\alpha\beta}^{rs} + \underline{Z}_{\alpha\beta\gamma}^{rs} \underline{e}_{\gamma}, \quad \text{i.e.,} \quad \underline{b}^{rs} = \underline{Z}_{\alpha\beta\gamma}^{rs} \underline{e}_{\gamma}, \quad (15)$$

\underline{Z}^{rs} being the transition hyper-polarizability tensor.

The last equation does not help us very much because of the almost complete lack of reliable experimental data on \underline{Z}^{rs} and $\underline{e}(t)$. However, under the conditions at which ordinary Raman spectra are measured, the spontaneous emission and the hyper-Raman effect are both unmeasurably weak. This indicates that, at least in the case of symmetry-allowed fundamental bands, the second term in Eq. (15) is negligible with respect to \underline{a}^{rs} . In order to simplify the further discussion, let us assume that the band in question is a strong fundamental and put

$$\underline{C}^{rs}(\tau) = \underline{S}^{rs}(\tau). \quad (16)$$

IV. Symmetry Properties of \underline{S}^{rs}

The tensor \underline{S}^{rs} describes the reorientation¹⁰ of the ellipsoid $\underline{a}^{rs}(t)$. As usual, let us write \underline{a}^{rs} in the form

$$\underline{a}^{rs}(t) = a^{rs} \underline{I} + \underline{\alpha}^{rs}(t), \quad (17)$$

where $a^{rs} = (1/3)\text{Tr } \underline{a}^{rs}(t)$. Since $\underline{\alpha}^{rs}(t)$ is a traceless tensor and a^{rs} is a time independent scalar,

$$\underline{S}_{\alpha\beta, \gamma\delta}^{rs}(\tau) = |a^{rs}|^2 \delta_{\alpha\beta} \delta_{\gamma\delta} + \mathcal{A}_{\text{rot}} [\alpha_{\alpha\beta}^{rs}(t) \alpha_{\gamma\delta}^{sr}(t+\tau)]. \quad (18)$$

Being a traceless symmetrical tensor of second rank, $\underline{\alpha}^{rs}$ belongs to the $j=2$ representation of the rotational group. The following linear combinations¹¹ of its coefficients behave under rotations of coordinates

like spherical functions $Y_{2,\mu}$:

$$\begin{aligned} F_0^{rs} &= \underline{\alpha}_{ZZ}^{rs} \\ F_{\pm 1}^{rs} &= \mp (2/6^{\frac{1}{2}}) (\underline{\alpha}_{ZX}^{rs} \pm i \underline{\alpha}_{ZY}^{rs}) \\ F_{\pm 2}^{rs} &= 6^{-\frac{1}{2}} (\underline{\alpha}_{XX}^{rs} - \underline{\alpha}_{YY}^{rs} \pm 2i \underline{\alpha}_{XY}^{rs}) . \end{aligned} \quad (19)$$

In an isotropic medium, a single correlation function $g^{rs}(\tau)$ is sufficient to describe the statistical reorientation of the tensor $\underline{\alpha}^{rs}$.

It holds that for any μ and ν

$$\mathcal{A}_{\text{rot}} [F_{\mu}^{rs}(t) F_{-\nu}^{rs}(t+\tau)] = (-)^{\mu} \delta_{\mu\nu} g^{rs}(\tau) . \quad (20)$$

It is useful to introduce the reduced correlation function $\chi^{rs}(\tau)$ defined as

$$\chi^{rs}(\tau) = g^{rs}(\tau)/g_0^{rs} ; \quad g_0^{rs} = g^{rs}(0) = (2/15) \text{Tr}(\underline{\alpha}^{rs} \underline{\alpha}^{sr}) . \quad (21)$$

The two independent components of \underline{S}^{rs} may then be written as

$$\begin{aligned} \underline{S}_{XX,XX}^{rs}(\tau) &= |\underline{a}^{rs}|^2 + g_0^{rs} \chi^{rs}(\tau) , \\ \underline{S}_{XY,XY}^{rs}(\tau) &= \frac{3}{4} g_0^{rs} \chi^{rs}(\tau) . \end{aligned} \quad (22)$$

Combining these Equations with (9), (10), and (16), one obtains

$$G_1^{rs}(\tau) = \underline{G}_{XX,XX}^{rs}(\tau) = |\underline{a}^{rs}|^2 C_{rs}(\tau) + g_0^{rs} C_{rs}(\tau) \chi^{rs}(\tau) , \quad (23a)$$

$$G_2^{rs}(\tau) = \underline{G}_{XY,XY}^{rs}(\tau) = \frac{3}{4} g_0^{rs} C_{rs}(\tau) \chi^{rs}(\tau) . \quad (23b)$$

V. Experimental Determination of $C_{rs}(\tau)$ and $\chi^{rs}(\tau)$

The functions $G_1^{rs}(\tau)$ and $G_2^{rs}(\tau)$ are connected with experimental band-shapes by the formulae (see Equations (3), (8), and (9))

$$G_i^{rs}(\tau) = c_r^{-1}(\nu_0^{rs})^{-4} \int_{-\infty}^{+\infty} (1-\nu/\nu_0^{rs})^{-4} I_i^{rs}(\nu) \exp(2\pi i \nu \tau) d\nu, \quad (24)$$

$i = 1, 2$

where

$$\begin{aligned} I_1^{rs}(\nu) &= I^{rs}(1, 0, 0; 1, 0, 0; \nu), \\ I_2^{rs}(\nu) &= I^{rs}(1, 0, 0; 0, 1, 0; \nu). \end{aligned} \quad (25)$$

Since it is very difficult to measure the absolute intensities of Raman bands we will avoid their use at the price that the values a^{rs} and g_0^{rs} will remain undetermined. Let us introduce the function

$$I_0^{rs}(\nu) = I_1^{rs}(\nu) - (4/3)I_2^{rs}(\nu) \quad (26)$$

and normalize¹² both $I_0^{rs}(\nu)$ and $I_2^{rs}(\nu)$ as follows

$$\tilde{I}^{rs}(\nu) = I^{rs}(\nu) / \int_{-\infty}^{+\infty} (1-\nu/\nu_0^{rs})^{-4} I^{rs}(\nu) d\nu. \quad (27)$$

It is easy to see that

$$\int_{-\infty}^{+\infty} (1-\nu/\nu_0^{rs})^{-4} \tilde{I}_0^{rs}(\nu) \exp(2\pi i \nu \tau) d\nu = c_{rs}(\tau) \quad (28)$$

and

$$\int_{-\infty}^{+\infty} (1-\nu/\nu_0^{rs})^{-4} \tilde{I}_2^{rs}(\nu) \exp(2\pi i \nu \tau) d\nu = c_{rs}(\tau) \chi^{rs}(\tau). \quad (29)$$

Dividing the second of these equations by the first, one obtains the function $\chi^{rs}(\tau)$.

The experimental bandshapes (25) and the simple mathematical procedure described by Eqs. (26)-(29) enable one to separate the reorientation processes from all other broadening mechanisms.

The band I_0^{rs} obviously represents the pure Q-branch, while I_2^{rs} comprises what in the case of a free molecule would be called O, P, R, and S branches. As $|c_{rs}(\tau)| < 1$ for any $\tau \neq 0$, the band I_0^{rs} is always narrower than the band I_2^{rs} . For highly symmetrical vibrations the band I_2^{rs} may be forbidden; in this case the function $c_{rs}(\tau)$ may still be

obtained from the band I_i^{rs} while the function $\chi^{rs}(\tau)$ is inaccessible.

If, on the other hand, the trace of the polarizability tensor is negligibly small (being accidental, this case is very rare) the separation of $\chi^{rs}(\tau)$ from $C_{rs}(\tau)$ is impossible.

VI. Vibrational Raman Bands of Rigid Molecules and Molecular Fragments

Let us first ask what exactly is to be included into the term 'reorientation processes'. Qualitatively, the answer is clear; the transformation (24) includes any process which in any way influences the tensor \underline{A}^{rs} , and the frequencies of which do not exceed substantially the width of the vibrational band.

If the molecule does not undergo internal rotations (for the present purposes, let us call such a molecule 'rigid'), the dominant processes will be the overall rotation and the vibrational energy transfer. In general, of course, the term 'reorientation' will include also free internal rotations and low-frequency torsional motions. Since a large-amplitude change of the molecular conformation may lead to a substantial change of the shape of \underline{A}^{rs} , the approximation Eq. (16) is hardly acceptable in such cases. These kinds of shape deformations of \underline{A}^{rs} have not been considered in Eq. (15); it is nevertheless evident that they may occasionally lead to quite large values of the tensor \underline{w}^{rs} .

From the preceding discussion it might seem that the theory developed in Sections IV and V applies only to the case of rigid molecules. This is not true since even in large molecules most vibrations are well localized and may be described as group vibrations of rigid molecular fragments. The treatment described in Section V provides extremely valuable information on the reorientation mobility of the molecular fragments in question. The limitation mentioned above thus applies only to delocalized vibrations

such as the chain vibrations of long linear molecules with regular structure.

The reduced correlation function

$$\chi^{rs}(\tau) \equiv \chi(\underline{\alpha}^{rs}; \tau)$$

depends on the shape of the tensor $\underline{\alpha}^{rs}$ as well as on its orientation with respect to the molecular system of coordinates. Since traceless symmetrical tensors form a five-dimensional linear manifold, it is possible to write any such tensor as a linear combination of five independent tensors $\underline{\beta}_i$ representing a base of the manifold:

$$\underline{\alpha}^{rs} = \sum_{i=1}^5 c_i^{rs} \underline{\beta}_i . \quad (30)$$

In the case of a rigid molecule (or fragment) the base $\underline{\beta}_i$ may be chosen as fixed with respect to the molecular frame; the coefficients c_i^{rs} are then time-independent and

$$\chi(\underline{\alpha}^{rs}; \tau) = \sum_{i=1}^5 \sum_{j=1}^5 c_i^{rs} c_j^{rs*} \chi_{ij}(\tau) , \quad (31)$$

where

$$\chi_{ij}(\tau) \equiv \chi(\underline{\beta}_i, \underline{\beta}_j; \tau) = \mathcal{A}_{\text{rot}} [\underline{\beta}_i(t) \underline{\beta}_j(t+\tau)] / [\text{Tr}(\underline{\beta}_i)^2 \text{Tr}(\underline{\beta}_j)^2]^{\frac{1}{2}} . \quad (32)$$

Since

$$\chi(k\underline{\beta}_i, k'\underline{\beta}_j; \tau) = \chi(\underline{\beta}_i, \underline{\beta}_j; \tau) = \chi_{ij}(\tau) , \quad (33)$$

we may limit ourselves to the normalized tensors and require

$$\sum_{i=1}^5 |c_i^{rs}|^2 = 1 . \quad (34)$$

Finally, the base $\underline{\beta}_i$ may be chosen to be orthogonal under the metric

$$\rho(\underline{\beta}_i, \underline{\beta}_j) \equiv \text{Tr}(\underline{\beta}_i \underline{\beta}_j^+) ; \quad (35)$$

this implies

$$\chi_{ij}(0) = \delta_{ij} . \quad (36)$$

With regard to the last Equation, it is not unreasonable to suppose that the cross-correlation functions $\chi_{ij}(\tau)$, $i \neq j$, are always small in comparison with $\chi_{ii}(\tau)$ so that

$$\chi_{ij}(\tau) \approx \chi_{ii}(\tau) \delta_{ij} . \quad (37)$$

In summary, we have just shown that the correlation function $\chi(\underline{\alpha}^{rs}; \tau)$ derived from any vibrational Raman band of a rigid molecule or molecular fragment is a linear combination of at most 15 independent functions $\chi_{ij}(\tau)$, $i, j=1, 2, 3, 4, 5$; in many practical applications this number may be reduced to 5 by neglecting all the cross-correlation functions $\chi_{ij}(\tau)$, $i \neq j$.

VII. Semiempirical Approximations

In spite of the restriction contained in the last paragraph of the preceding Section, many molecules do not have a sufficient number of Raman active vibrational bands distributed in such a way that their mutual overlap would not obstruct the measurement of their natural shapes. It means that additional information is needed if the reorientation process of all molecular second-rank tensors is to be characterized on the basis of Raman data.

In many cases, for example, the symmetry of the molecule (or fragment) in question leads to a substantial simplification of the problem. Another source of additional information may be a reasonable approximation regarding the reorientation process itself. As a particular example, the case of a

continuous anisotropic diffusion will be mentioned in this Section. It is of course necessary to underline that this particular model may be satisfactory in some cases and unacceptable in others. The same may be said of all other common approximations such as those assuming finite rotational jumps. Up to now there is no sufficiently general theory valid for all molecular systems.

The continuous diffusion model was first developed by Furry¹³ for isotropic Brownian motion. A model of continuous anisotropic diffusion had been developed by Perrin¹⁴ and, independently, by Favro¹⁵ who had generalized Furry's treatment. A detailed mathematical discussion of the model exceeds the scope of this paper; the reader interested in this problem can find most of the work done in the fundamental paper by Favro¹⁵. The important result is that the reorientation of a rigid molecule (fragment) is described by the rotational diffusion tensor \underline{D} . The correlation function $\chi(\underline{\alpha};\tau)$ is then uniquely defined by the shapes and the mutual orientation of the two tensors \underline{D} and $\underline{\alpha}$. This amounts to 7 independent numerical parameters, three of which (the principal values of \underline{D}) are common to all correlation functions which refer to the same molecule (fragment). Combined with the symmetry restrictions mentioned above, this result makes the complete characterization of the molecular reorientation process by means of Raman spectra quite feasible.

VIII. Discussion and Further Perspectives

The main advantage of Raman Spectroscopy lies in the fact that it consists of two different contributions--scalar and tensor--the angular dependences of which are different. As shown in Section V, this enables one to separate from each other the scalar (Σ) and the second-rank tensor

(Δ) processes. If the scalar processes are dominated by the vibrational energy transfer then their influence on Raman lines must be identical with that on IR lines. Combined IR and Raman measurements could then provide relatively reliable information on the vector (Π) line-broadening mechanisms. The comparison between vector and tensor processes represents a sensitive and independent check of the model chosen (e.g., the continuous model of rotational diffusion) for the calculation of correlation functions. For the same reason, it might be also useful to study the lineshapes of hyper-Raman lines which consist of mutually separable vector and third-order tensor contributions.

The Δ processes belong to the dominant ones also in other spectroscopic techniques like NMR or ESR. Although the broadening mechanism in high-resolution NMR is well understood either for isolated nuclei¹⁶ either for coupled nuclear systems^{17, 18}, these spectroscopical methods are less suitable for the study of Δ processes than the Raman scattering because of their sensitivity to too many details of the molecular geometry and of the coupling scheme of the nuclear system. The Raman (and IR) data could thus serve as a precious source of empirical data for the other spectroscopical techniques. Furthermore, some approximations currently used in magnetic resonances (e.g., the exponential decay approximation¹⁷ or the assumption of identical reduced correlation functions¹⁷) may be relatively easily checked by means of a careful study of Raman spectra.

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References

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- ¹ G. Placzek, E. Teller, Z. Physik 81, 209 (1933).
 - ² R. G. Gordon, J. Chem. Phys. 43, 1307 (1965).
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 - ⁵ The components of vector and tensor quantities are denoted by Greek indices while small Latin indices refer to vibrational eigenstates. The capital letter indices X, Y, and Z are used to denote tensor components in a materially fixed laboratory coordinate system. The summation convention is adopted to the dummy Greek indices. No distinction is made between the covariant and the contravariant components because the adopted coordinate systems are supposed to be orthogonal.
- The δ -tensors are defined as usual by means of the completely skew-symmetric tensors $\epsilon_{\alpha\beta\gamma}$, i.e., $\delta_{\alpha\beta}^{\gamma\delta} = \epsilon_{\alpha\beta\varphi} \epsilon_{\gamma\delta\varphi}$ $\delta_{\alpha\beta} = \frac{1}{2} \delta_{\alpha\beta}^{\gamma\delta}$.
- ⁶ W. Heitler, The Quantum Theory of Radiation (Clarendon, Oxford, England, 1957).
 - ⁷ If one assumes complete separation of the vibrational degrees of freedom from all the others (an assumption inherently contained in Eq. (1)), the effect of any such event which appeared at a time t_0 is equivalent to putting $Q^{rs}(t) = 0$ for $t > t_0$.
 - ⁸ Several statistical averaging operators are used in this paper. Each of them is characterized by the region of the configurational space of molecular ensemble to which it applies. So $\mathcal{A}_{\text{rot}}(\mathcal{A}_{\text{tr}})$ averages only over the rotational (translational) degrees of freedom of the particular molecule. The operator which results from \mathcal{A} by excluding the translations and the vibrations of the molecule in question is denoted as \mathcal{A}' .
 - ⁹ D. N. Zubarev, Soviet Physics Uspekhi 3, 320 (1960).
 - ¹⁰ When the random character of the process is emphasized, the term reorientation is used instead of the term rotation. Since pure rotation is a limiting case of the reorientation process, any acceptable theory of the latter must necessarily also embrace the former.
 - ¹¹ L. D. Landau, E. M. Lifshitz, Quantum Mechanics (Chapter XIV, second edition, Addison-Wesley, Reading, Massachusetts, 1965).
 - ¹² Notice that while the knowledge of absolute intensities is not required, the ratio $I_2^{rs}(\nu)/I_1^{rs}(\nu)$ has a basic importance and must not be distorted by such interfering effects as polarization-dependent losses of the beam intensity on lenses, mirrors, and other surfaces.

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13. Abstract:

It has been shown that the shapes of vibrational Raman bands, measured with both parallel and crossed nicols, may serve as a tool for the study of the reorientation of rigid molecules (or molecular fragments) even if other line-broadening mechanisms are not negligible. The theory, developed for the case of isotropic media (including dense gases, liquids, and some molecular solids), holds independently of the shape of the molecules; the only requirement is that the studied band must be related to a vibration which is sufficiently localized to the individual molecule (molecular fragment).

Any vibrational Raman band provides, in principle, enough information for a complete characterization [by means of correlation function $\chi(\alpha_{\text{ig}}^{\text{ig}}; \tau)$] of the reorientation of the corresponding transition polarizability tensor $\alpha_{\text{ig}}^{\text{ig}}$. An exhaustive characterization of the reorientation properties of all second-rank molecular quantities is shown to be probably out of the reach of Raman spectroscopy except when the molecule (molecular fragment) has a high symmetry and/or a specific model of the reorientation process is accepted.